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Coherent control of attosecond emission from aligned molecules

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Controlling attosecond electron wavepackets and soft x-ray pulses represents a formidable challenge of general implication to many areas of science¹⁻⁴. A strong laser field interacting with atoms or molecules drives ultrafast intra-atomic/molecular electron wavepackets on a subfemtosecond timescale, resulting in the emission of attosecond bursts of extreme ultraviolet (XUV) light^{5,6}. Controlling the intra-atomic/molecular electron dynamics allows steering the attosecond emission^{7,8}. Here we perform a coherent control in linear molecules, where the interaction of the laser-driven

electron wavepacket with the core leads to quantum interferences⁹⁻¹². We demonstrate that these interferences can be finely controlled by turning the molecular axis relative to the laser polarization, i.e. changing the electron recollision angle. The wavepacket Coulombic distortion modifies the spectral phase jump measured in the XUV emission. Our attosecond control of the interference results in an attosecond pulse shaping, useful for future applications in ultrafast coherent control of atomic and molecular processes. High Harmonic Generation in gases^{13,14} is a spectacular process arising when a strong laser field tunnel ionizes an atom/molecule, creating an attosecond electron wavepacket that is subsequently accelerated and driven back to the core by the laser field^{15,16}. It may then recombine to the ground state, releasing its accumulated kinetic energy in the form of an attosecond burst of XUV light. In a multi-cycle laser field, this process is repeated every half-cycle leading to a train of attosecond pulses whose spectrum contains only the odd harmonics of the laser frequency. The precise characterization of this attosecond emission gives insight into the ultrafast electron dynamics¹⁷. A control of the *continuum* electron dynamics –and of the resulting XUV emission- can be performed by shaping the laser field, through a time-varying polarization⁷ or a multicolour superposition⁸. Our approach is to control coherently the *recombination* step in linear molecules, when the returning electron wavepacket interacts with the multi-centre core, leading to quantum interferences⁹⁻¹².

A simple way to describe such interferences in diatomic molecules is the two-center interference model^{9,18}: the recolliding electron wavepacket is modelled by a plane wave $\Psi_c \propto \exp[i\mathbf{k}\mathbf{r}]$, and the ground state (the Highest Occupied Molecular Orbital, HOMO) by a linear combination of atomic orbitals. For an antisymmetric combination:

$\Psi_0 \propto \Phi_0(\mathbf{r} - \mathbf{R}/2) - \Phi_0(\mathbf{r} + \mathbf{R}/2)$, where \mathbf{R} is the internuclear vector, the recombination dipole moment in the velocity form¹⁹ reads:

$$\langle \Psi_c | \mathbf{p} | \Psi_0 \rangle \propto i \mathbf{k} \sin(\mathbf{k} \mathbf{R} / 2) \langle \exp[i\mathbf{k}\mathbf{r}] | \Phi_0 \rangle, \quad (1)$$

where \mathbf{p} is the dipole momentum operator.

A destructive interference is obtained at $\mathbf{kR}/2 = n\pi$, i.e. when

$$R\cos\theta = n\lambda_e, \quad (2)$$

where θ is the angle between molecular axis and electron propagation direction given by the laser polarization, n is an integer and λ_e is the electron de Broglie wavelength. The molecule then behaves like a two-point emitter whose emissions are dephased due to i) the path difference between the centers, ii) the symmetry of the orbital.

The CO₂ molecule, although triatomic, provides good conditions for observing this quantum interference. Indeed, its HOMO is a Π orbital dominated by the antisymmetric combination of two p orbitals centred on the O atoms. Moreover, the O-O distance ($R_{O-O} = 4.39$ a.u.) corresponds to an electron wavelength typical of the harmonic generation process. The recombination dipole moment exhibits a clear minimum close to that expected from equation (2) – however for $R = 3.9$ a.u. $< R_{O-O}$ (see Fig. 1). This deviation is due to a non-negligible contribution to the HOMO from the d_{xy} carbon orbital, and also to a lesser extent from the d_{xy} oxygen orbitals whose symmetry does not correspond to the interference condition (2).

The electron de Broglie wavelength $\lambda_e = 2\pi/k$ is directly related to the energy of the emitted photon by: $\hbar^2 k^2 / 2m_e = \hbar\omega$ (this heuristic relation predicts an interference position that agrees well with that obtained from accurate simulations^{10,19} for H₂⁺). The destructive interference will thus appear in the harmonic spectrum as a clear minimum at a specific harmonic order (harmonic 23 for $\theta = 0$). Recent measurements in aligned CO₂ molecules have given indications of the presence of such a minimum^{11,12}. However, those observations rely only on spectral amplitude measurements, and hence could be explained by the interplay between the distribution of the partially aligned molecules and the angular dependence of the harmonic yield²⁰.

Our analysis is based on the measurements of both amplitude and phase of the harmonic emission from aligned molecules. The spectral phase, though more difficult to measure, contains important information on the interference process. In particular, a phase jump of π is expected at the position of destructive interference^{9,18}. Indeed, the sign of the dipole moment in Fig. 1 changes at the amplitude minimum. The harmonic phase is also a crucial element for recovering the symmetry of the molecular orbitals in the tomographic reconstruction procedure²¹. Finally, it gives insight into the ultrafast electron dynamics and allows the reconstruction of the attosecond emission temporal profile.

We have characterized the harmonic emission from nonadiabatically aligned²² CO₂ molecules (see Methods). The RABITT technique^{5,17,23} gives access to the relative phases of neighbouring harmonics, and thus to the group delay, also called emission time:

$$t_e(\omega_{q+1}) := \frac{\partial \varphi}{\partial \omega} \approx \frac{\varphi_{q+2} - \varphi_q}{2\omega_0}.$$

In rare gas atoms, this emission time varies linearly with the harmonic order in the plateau region, and coincides with the recollision time of the electron trajectories¹⁷. The resulting frequency chirp of the harmonic emission is a direct signature of the continuum electron dynamics. This is illustrated in Fig. 2a for krypton, which has a similar ionization potential as CO₂ ($I_p(\text{Kr}) = 14.00$ eV, $I_p(\text{CO}_2) = 13.77$ eV). Such a reference atom can be used to calibrate the recolliding electron wavepacket^{21,24}: one expects that the first two steps of the harmonic emission process (tunnel ionization and continuum dynamics) will be similar in the two gases (except for the ionisation angular dependence; see Methods). Indeed, the emission times of the CO₂ molecules aligned perpendicularly to the laser field match very closely those of Kr (Fig. 2a). However, for parallel alignment, a strong deviation is observed between harmonics 25 and 29. Integrating the difference between the emission times in CO₂ and in Kr gives the phase associated with the recombination process only (Fig. 2b). It presents a clear jump

starting at harmonic 25, close to the prediction of the dipole calculation for the destructive interference. However, there are two remarkable features that are generic to all our measurements. First, the total phase jump is 2.7 rad in this data set, and not π (value averaged over 8 measurements: 2.0 ± 0.6 rad). Second, this jump is not step-like but spread over three harmonic orders.

Such deviations cannot be explained by an imperfect experimental alignment: the convolution of the rotational wavepacket angular distribution with the dipole in Fig. 1b (both real-valued functions) would only induce a shift of the interference position but neither a spread nor a reduced value of the phase jump that both correspond to a complex dipole value. Such deviations appeared in early simulations^{9,18} performed in H_2^+ and H_2 single molecules: a reduced phase jump of 2.7 rad spread over 5 orders was found in H_2^+ and even stronger deviations appeared in H_2 . A recent dipole calculation replacing the plane waves in equation (1) by two-center Coulomb wavefunctions has reproduced this behaviour¹⁹: the incorporation of the Coulomb binding potential of the atomic centers modifies the prediction of two-center interference, in particular the shape of the phase jump. Our measured phase jump would thus contain a direct signature of the Coulombic distortion of the recolliding electron wavepacket, uncovered by the high sensitivity of the quantum interference.

We have performed careful measurements of the phase jump as a function of the alignment angle (Fig. 3b). It reaches 2 rad for angles below 30° and quickly decreases to 0 with increasing angle. This may correspond to a shift to harmonic orders outside our accessible spectral range, in agreement with the dipole calculation in Fig. 1b. The harmonic amplitudes (Fig. 3a), normalized to those measured in krypton, exhibit a clear minimum around H23-25 at small angles, which disappears at large angles. The consistency of the amplitude and phase data is excellent and demonstrates a fine control of the quantum interference by turning the molecular axis. Note that the exact position of the interference may change significantly with

intensity (phase jump for parallel alignment starting at H25 in Fig. 2b instead of H23 in Fig. 3b due to the larger intensity), as also observed in recent amplitude measurements²⁵. This additional deviation from the two-point emitter model may explain the different interference positions reported in Ref. 11 (H25) and Ref. 12 (H33).

The temporal characteristics of the quantum interference reveal an unexpected behaviour. With the measured amplitudes and phases, we reconstruct the temporal profile of the XUV emission^{5,17,23}, and thus the acceleration of the dipole moment that mirrors the intra-molecular electron dynamics. The temporal profile corresponding to orders 17-23 below the phase jump is very similar to that of krypton and does not vary significantly with the alignment angle (Fig. 4a). In contrast, the emission of harmonics 23-29 undergoing the phase jump is delayed in time with respect to krypton by 150 as for small angles and gradually converges to it with increasing angle (Fig. 4b). This delay is due to the quantum interference in the recombination process, and not to the transit time of the electron wavepacket between the two oxygen atoms, that is twice as small. The spreading of the phase jump over 3 harmonic orders shifts the corresponding emission times to larger values (Fig. 2a), resulting in a delayed attosecond emission (Fig. 4b) with a barely modified pulse shape (slightly reduced FWHM as compared to perpendicular alignment). This surprising result is a consequence of both the spreading and the occurrence of the quantum interference in the harmonic cutoff. There, the amplitude drops quickly with order, so that the destructive interference between spectral components on either side of the phase jump is not efficient enough to distort the temporal profile. The pulse reconstruction using the experimentally measured phases but assuming equal amplitudes for harmonics 17-29, results in a strong distortion with the expected double peak (Fig. 4c). The strongest distortion of the pulse (double peak with zero amplitude in between) would be obtained for a step-like π phase jump positioned in the middle of a flat spectrum.

The full potential of pulse shaping offered by the measured phase jump can be reached by performing simultaneously an amplitude shaping. For instance, a clean double pulse could be obtained either using thin filters, or by placing the phase jump in the plateau region of the harmonic spectrum, which should be possible by generating with higher intensity and shorter pulses. By combining amplitude control and phase control (since the position and height of the phase jump depend on molecular structure and orientation), we extend the possibility of coherent quantum control to the XUV and attosecond domain. For example, coherent transient enhancement of a resonant transition²⁶ could be performed if the phase jump of $\approx \pi$ is placed at the transition energy. The below- and above-resonance contributions to the excited state population then interfere constructively.

We have shown how molecular structure and orientation affect the attosecond shape of the total (continuum+bound) electron wavepacket during recollision. Additional effects could also play a role in shaping the wavepacket:

- i) interplay of the molecular potential with the strong laser field (Coulomb-laser coupling)²⁷,
- ii) Π symmetry of the CO₂ HOMO reflected in the structure of the recolliding electron wavepacket²⁸, iii) ionisation dynamics involving many orbitals²⁸ and in particular orbitals below the HOMO²⁵, iv) exchange effects with core electrons^{29,30}. At present, the relative importance of these factors is unknown. Our measurements thus provide crucial information to benchmark improved models of the interaction of molecules with strong laser fields.

Our demonstrated control on attosecond time scale provides a way to generalize the use of the continuum electron wavepacket as a probe of molecular systems, in particular for accurate *ab initio* tomographic imaging of molecular orbitals. The XUV spectral phase could also be used to probe Coulombic recolliding electron wavepackets. Finally, the control of the attosecond emission is a further step toward the XUV pulse shaping that will open a new class of experiments, such as XUV coherent control of atomic and molecular systems.

METHODS

We used the LUCA laser facility, which delivers to our experiment infrared pulses of 50 fs duration and up to 30 mJ in energy. A supersonic gas jet of CO₂, cooled in expansion to rotational temperature of about 90 K, provides the molecular sample. An aligning laser pulse focused up to 5×10^{13} W/cm² with a lens of 1 m focal length creates a rotational wave packet in the medium²². This wave packet periodically rephases, giving at the revival times a strong molecular alignment along the polarization direction (angular distribution of the rotational wavepacket confined in a cone angle of $\sim 20^\circ$). At the half revival time (equal to half the rotational period of the molecule), a second, more intense laser pulse of approximately 1×10^{14} W/cm² generates high harmonics from the aligned molecules. A micrometric motorized translation stage is used to control the delay, and the angle between the axis of molecular alignment and the polarization of the generating beam is monitored by a motorized half-wave plate inserted in the aligning beam. To implement the “Reconstruction of Attosecond Beating by Interference of Two-photon Transition” (RABITT) technique, we need a third, weaker pulse of intensity about 10^{11} W/cm², whose synchronization with the generating pulse is controlled by a piezoelectric translation stage. After harmonic generation, a diaphragm blocks the aligning and generating beams. A broadband toroidal mirror under grazing incidence focuses the harmonics and dressing beam in a detecting neon jet placed in the source volume of a magnetic bottle electron spectrometer (see Ref. 17, Fig. 2 for the phase measurement part of the setup).

This demanding setup requires precise alignment of three laser beams (aligning, generating and dressing) whose intensities, delays and polarization should be controlled independently. In particular, the interferometric stability needed by the RABITT measurements must be

preserved for more than one and a half hour to perform the acquisition of the data shown in Fig. 3.

The RABITT technique measures the derivative of the harmonic phase, not the phase itself.

To get a phase reference for Fig. 2b and Fig. 3b, we assume that the phase of harmonic 15 generated in CO₂: i) does not vary with angle, and ii) for convenience, is the same as the one in Kr. The first assumption is supported by recent interferometric experiments²⁵

demonstrating a very weak angular dependence of the phase of low harmonics in CO₂.

Within the plane wave approximation, the transition dipole moment $d_{CO_2}(\omega, \theta)$ between a continuum state and the CO₂ HOMO can be directly related to the harmonic intensity ratio

$\frac{S_{CO_2}(\omega, \theta)}{S_{Kr}(\omega)}$ and phase difference $\varphi_{CO_2}(\omega, \theta) - \varphi_{Kr}(\omega)$ measured in CO₂ and the krypton

reference gas using²¹:

$$d_{CO_2}(\omega, \theta) = \langle \Psi_c | \mathbf{p} | \Psi_{CO_2} \rangle = \sqrt{\frac{P_{Kr}}{P_{CO_2}(\theta)}} \sqrt{\frac{S_{CO_2}(\omega, \theta)}{S_{Kr}(\omega)}} \exp[i(\varphi_{CO_2}(\omega, \theta) - \varphi_{Kr}(\omega))] \langle \Psi_c | \mathbf{p} | \Psi_{Kr} \rangle,$$

where Ψ_{CO_2} is the CO₂ HOMO wavefunction, Ψ_{Kr} is the 4p orbital of Krypton, Ψ_c is a plane wave $\exp[i\mathbf{k}(\omega)\mathbf{r}]$ propagating along the laser polarization direction, P_{CO_2} is the angle-dependent ionization yield of CO₂ and P_{Kr} is the ionization yield of Kr. Since the Kr dipole is real valued and presents a smooth behaviour, it does not modify significantly the structures observed in Fig. 3 that can thus be attributed to the CO₂ dipole. Note finally that the above formula does not apply at $\theta=0$ and 90° where the ionization is suppressed in CO₂ due to the HOMO symmetry.

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Author contributions

P.S. with B.C, H.M .and P.M. planned the project. W.B., H.M., P.B., P.M., B.C. and P.S. designed and installed the experiment. W.B. and S.H., with assistance of H.M., P.B., G.W., M.S., L.J.F., P.M. and P.S. performed the measurements. W.B., S.H., H.M. and P.S. analyzed the data. R.T., J.C. and A.M. performed the dipole simulations. All authors discussed the results and contributed to the final manuscript. W.B. and S.H. contributed equally to this work.

Competing financial interests

The authors declare that they have no competing financial interests.

References

1. Drescher, M. et al. Time-resolved atomic inner-shell spectroscopy. *Nature* **419**, 803-807 (2002).
2. Remetter, T. et al., Attosecond electron wave packet interferometry. *Nature Phys.* **2**, 323-326 (2006).
3. Baker, S. et al. Probing Proton Dynamics in Molecules on an Attosecond Time Scale. *Science* **312**, 424-427 (2006).
4. Cavallieri, A. et al. Attosecond spectroscopy in condensed matter. *Nature* **449**, 1029-1032 (2007).

5. Paul, P. M. et al. Observation of a Train of Attosecond Pulses from High Harmonic Generation. *Science* **292**, 1689- 1692 (2001).
6. Hentschel, M. et al. Attosecond metrology. *Nature* **414**, 509-513 (2001).
7. Sola, I. et al. Controlling attosecond electron dynamics by phase-stabilized polarization gating. *Nature Phys.* **2**, 319-322 (2006).
8. Pfeifer, T. et al. Single attosecond pulse generation in the multicycle-driver regime by adding a weak second-harmonic field. *Opt. Lett.* **31**, 975-977 (2005).
9. Lein, M., Velotta, R., Marangos, J. P. & Knight, P. L. Role of the Intramolecular Phase in High-Harmonic Generation. *Phys. Rev. Lett.* **88**, 183903 (2002).
10. Lagmago Kamta, G. & Bandrauk, A.D. Three-dimensional time-profile analysis of high-order harmonic generation in molecules: Nuclear interferences in H_2^+ . *Phys. Rev. A* **71**, 053407 (2005).
11. Kanai, T., Minemoto, S. & Sakai, H. Quantum interference during high-order harmonic generation from aligned molecules. *Nature* **435**, 470-474 (2005).
12. Vozzi, C. et al. Controlling Two-Center Interference in Molecular High Harmonic Generation. *Phys. Rev. Lett.* **95**, 153902 (2005).
13. McPherson, A. et al. Studies of multiphoton production of vacuum-ultraviolet radiation in the rare gases. *J. Opt. Soc. Am. B* **4**, 595-601 (1987).
14. Ferray, M. et al. Multiple-harmonic conversion of 1064 nm radiation in rare gases. *J. Phys. B* **21**, L31-L35 (1988).
15. Corkum, P. B. Plasma perspective on strong field multiphoton ionization. *Phys. Rev. Lett.* **71**, 1994-1997 (1993).
16. Schafer, K. J., Yang, B., DiMauro, L. F. & Kulander, K. C. Above threshold ionization beyond the high harmonic cutoff. *Phys. Rev. Lett.* **70**, 1599-1602 (1993).

17. Mairesse, Y. et al. Attosecond Synchronization of High-Harmonic Soft X-rays. *Science* **302**, 1540-1543 (2003).
18. Lein, M., Hay, N., Velotta, R., Marangos, J. P. & Knight, P. L. Interference effects in high-order harmonic generation with molecules. *Phys. Rev. A* **66**, 023805 (2002).
19. Ciappina, M. F., Chirila, C. C. & Lein, M. Influence of Coulomb continuum wave functions in the description of high-order harmonic generation with H_2^+ . *Phys. Rev. A* **75**, 043405 (2007).
20. Le, A.-T., Tong, X.-M. & Lin, C. D. Evidence of two-center interference in high-order harmonic generation from CO_2 . *Phys. Rev. A* **73**, 041402 (2006).
21. Itatani, J. et al. Tomographic imaging of molecular orbitals. *Nature* **432**, 867-871 (2004).
22. Rosca-Pruna, F. & Vrakking, M. Experimental Observation of Revival Structures in Picosecond Laser-Induced Alignment of I_2 . *Phys. Rev. Lett.* **87**, 153902 (2001).
23. Wabnitz, H. et al. Generation of attosecond pulses in molecular nitrogen. *Eur. Phys. J. D* **40**, 305-311 (2006).
24. Levesque, J., Zeidler, D., Marangos, J. P., Corkum, P. B. & Villeneuve, D. M. High Harmonic Generation and the Role of Atomic Orbital Wave Functions. *Phys. Rev. Lett.* **98**, 183903 (2007).
25. Mairesse, Y., Dudovich, N., Smirnova, O., Patchkovski, S., Zeidler, D., Levesque, J., Ivanov, M. Yu., Villeneuve, D.M., Corkum, P.B., Interferometric measurements of molecular structure, *International workshop on Attosecond Physics*, Dresden, 2007.
26. Dudovich, N., Oron, D. & Silberberg, Y. Coherent transient enhancement of optically induced resonant transitions. *Phys. Rev. Lett.* **88**, 123004 (2002).
27. Smirnova, O., Mouritzen, A. S., Patchkovskii, S. & Ivanov, M. Yu. Coulomb–laser coupling in laser-assisted photoionization and molecular tomography. *J. Phys. B* **40**, F197-F206 (2007).

28. Xie, X. et al. Subcycle dynamics in the laser ionization of molecules. *Phys. Rev. A* **76**, 023426 (2007).
29. Patchkovskii, S., Zhao, Z., Brabec, T. & Villeneuve, D. M. High Harmonic Generation and Molecular Orbital Tomography in Multielectron Systems: Beyond the Single Active Electron Approximation. *Phys. Rev. Lett.* **97**, 123003 (2006).
30. Zhao, Z., Yuan, J. & Brabec, T. Multielectron signatures in the polarization of high-order harmonic radiation. *Phys. Rev. A* **76**, 031404 (2007).

Figure Captions

Figure 1 Theoretical dependence of the CO₂ recombination dipole on the angle and energy of the free electron plane wave. Transition matrix element $\langle \exp[i\mathbf{k}\mathbf{r}]|\mathbf{p}|\Psi_0 \rangle$ where $\Psi_0 = \Psi_0(\theta, \mathbf{r})$ is the HOMO of CO₂, shown in polar coordinates as a function of the angle θ (deg) between the electron wavevector \mathbf{k} and the molecular axis, and the kinetic energy $k^2/2$ (atomic units) of the electron at recollision. **a**, In Ψ_0 , only the p orbitals of the oxygen atoms are included. The dipole moment changes sign when the recollision angle θ follows equation (2) with $n = 1$ and $R = 4.3$ a.u. (dotted line). **b**, Total Ψ_0 as computed with GAMESS (Hartree-Fock calculation). The non-negligible contribution of the d_{xy} (x along the internuclear axis) carbon orbital ($\sim 7\%$), and also to a lesser extent of the d_{xy} oxygen orbitals ($\sim 2\%$), shifts the position of the interference to higher energy (equivalent to smaller R in equation (2): the prediction for $R = 3.9$ a.u. is shown in dashed line). The dipole contribution of the d_{xy} carbon orbital obviously does not present any interference. As for the d_{xy} oxygen orbitals, they contribute to the total HOMO as a symmetric combination and thus give rise to a destructive interference following: $R \cos \theta = (n - 1/2)\lambda_e$. The sum of these different terms leads to the observed deviation.

Figure 2 Experimentally measured phase of the harmonic emission from aligned CO₂ molecules. **a**, Harmonic emission time, i.e. frequency-derivative of the spectral phase, for molecules aligned parallel (○) and perpendicular (△) to the laser polarization, and for krypton atoms (■), under the same generating conditions (intensity of 1.25×10^{14} W/cm²).

The error bars indicate the accuracy of the relative phase determination (standard deviation of the phase within the FWHM of the $2\omega_0$ peak in the RABITT trace Fourier transform).

Krypton and perpendicularly aligned CO₂ present the same linear dependence of the emission times, corresponding to the free electron wavepacket dynamics in the continuum¹⁷. The emission from molecules aligned parallel to the laser exhibits an additional delay between harmonics 25 and 29, corresponding to a rapid increase of the spectral phase. **b**, Difference of spectral phases ϕ between CO₂ molecules and krypton. Using this reference atom, the subtraction uncovers the phase solely due to the recombination process in the molecule. The phases are obtained from the data shown in panel **a** by the rectangular integration method. To show the relative phase at harmonic 31, we assumed the emission time at $30\omega_0$ of krypton (that could not be measured due to the low signal in the cutoff) to be equal to that of perpendicularly aligned CO₂ (measured thanks to the slightly higher cutoff). See Methods for the choice of the phase zero.

Figure 3 Experimental spectral intensity and phase of the CO₂ harmonic emission normalized by that of Kr. CO₂ harmonic intensity and phase (measured for molecule angles from 90° to 0°) normalized to the krypton data taken under the same experimental conditions (intensity of 0.95×10^{14} W/cm²). In order to prevent the dispersion effects due to the larger ionization rate of Kr, the corresponding data were taken at lower pressure (25 Torr vs. 60 Torr for CO₂) ensuring good phase matching conditions. The dashed lines are the same as the one

shown in Fig. 1b converted to harmonic order. The relation between the measured data and the recombination dipole moment is given in the Methods section. **a**, Intensity ratio vs. alignment angle θ (measured in steps of 5°) and harmonic order q . The ratio is not corrected for the different pressures. A clear intensity minimum is measured around harmonic 23 for $\theta = 0$ that disappears when the molecule is rotated. **b**, Spectral phase difference (as in Fig. 2b), measured in steps of 10° . A phase jump of 2 rad is observed at the same position as the intensity minimum.

Figure 4 Attosecond dynamics of the harmonic emission from aligned CO₂ molecules.

Intensity of a typical attosecond pulse in the generated train mapped as a function of the alignment angle θ and time t , with $t = 0$ at the maximum of the generating field. This dynamics is reconstructed from the spectral information in Fig. 3. Circles give the peak position of the pulse for ten θ values in a series of RABITT scans, and the error bars represent the standard deviation of the emission time of sideband 16, indicating the error in absolute timing of the attosecond pulses¹⁷. Grey and dashed white lines indicate the positions of peak and half-maximum, respectively, of the attosecond pulse generated in krypton under the same experimental conditions. **a**, Using harmonics 17-23, located below the phase jump. The attosecond pulses generated in CO₂ and krypton are the same, with a duration of 320 as FWHM. **b**, Using harmonics 23-29, undergoing the phase jump. For the parallel alignment ($\theta = 0^\circ$), the pulse is shifted by 150 as due to the phase jump and gradually moves to the same timing as krypton as the molecules are rotated towards the perpendicular alignment. **c**, Time profile for harmonics 17-29 assuming constant spectral amplitudes for $\theta = 0^\circ$ (black) and $\theta = 90^\circ$ (red). Note that we shifted the absolute timing of the pulses in **a**, **b** and **c** with respect to the generating field by +200 as. All emission times in this series including the Kr reference data were measured to be 200 as too low with respect to the data in Fig. 2 and to previous

findings¹⁷. However the atto chirp (slope of the emission time vs. frequency) in both Figs. 2 and 4 was as expected for the intensities used¹⁷. The small shift of time reference is presumably due to macroscopic effects (dispersion during propagation) and is here compensated for in order to present the single atom/molecule response.





